The transitioning feature between uncooked and cooked cowpea seeds studied by the mechanical compression test

Ekoué, T., Osseyi, E., Claire, M. D. & Ako, K.

Author post-print (accepted) deposited by Coventry University's Repository

Original citation & hyperlink:

Ekoué, T, Osseyi, E, Claire, MD & Ako, K 2021, 'The transitioning feature between uncooked and cooked cowpea seeds studied by the mechanical compression test', Journal of Food Engineering, vol. 292, 110368.

https://dx.doi.org/10.1016/j.jfoodeng.2020.110368

DOI 10.1016/j.jfoodeng.2020.110368

ISSN 0260-8774

Publisher: Elsevier

NOTICE: this is the author's version of a work that was accepted for publication in Journal of Food Engineering. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published in Journal of Food Engineering, 292, (2021) DOI: 10.1016/j.jfoodeng.2020.110368

© 2021, Elsevier. Licensed under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International http://creativecommons.org/licenses/by-nc-nd/4.0/

Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.

This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.

The transitioning feature between uncooked and cooked cowpea seeds studied by the mechanical compression test

Authors and affiliations:

Ekoué TEKO^a, Elolo OSSEYI^a, Claire D. MUNIALO^b, Komla AKO*c,d

- a) Département des sciences des Aliments et Technologie Agroalimentaire (SATA), ESTBA-UL B.P.1515-Lomé (TOGO)
- b) School of Life Sciences, Coventry University, Priory Street, Coventry, CV1 5FB, UK
- c) Univ. Grenoble Alpes, LRP, F-38000 Grenoble, France
- d) CNRS, LRP, F-38000 Grenoble, France

*Corresponding author: komla.ako@univ-grenoble-alpes.fr; akokomla@hotmail.com

Abstract:

Mechanical tests can allow for the mimicking of the textural attributes of foods as perceived by humans. Here we report on the use of the mechanical compression test to study the reactions underlying the cooking of the cowpea seeds (beans) until doneness. The creep test was applied to deal with the time dependence of the strain, $\varepsilon(t)$, at a constant force and to derive the elastic, K_e and viscosity, K_v indices for the different heating times. The results, $\varepsilon(t)$, were fitted using mostly a stretched exponential with a linear asymptotic (time) function. The flow rate (ω) and the strain (ε) are the constants of the asymptotic function. Both viscoelastic indices decreased strongly before the first 30 min (from 562 N to 14 N for K_e and from 5.4.10⁶ N.s to 0.11.10⁶ N.s for K_v), but from 30 to 75 min \pm 3 min, K_e remained almost constant (\sim 14 N) while K_v increases (from 0.11.10⁶ to 0.24.10⁶ N.s). Both viscoelastic indices decreased strongly again after 75 min \pm 3 min (from 14 N and 0.24.10⁶ N.s for K_e and K_v respectively). The heating time dependence of the viscoelastic indices clearly reflects the cowpeas beans transitioning to the

cooked state and this may be correlated directly to the kinetic of water absorption, starch gelatinization and protein denaturation. This would correlate not only to the cooking time but also to the nutrient quantity balance. The results from this study shows that the samples' mechanical properties with the simmering time are correlated with the cooking reactions.

Keywords: Cowpea(s); texture; gelatinization; yielding; stiffness; cooking time

1. Introduction

Cooking is a practice that requires knowledge and technical skills for controlling the food transformation particularly its texture and flavor until the food is considered as ready for consumption. Many vegetables such as fruits, legumes, roots and seeds, are edible uncooked or cooked. Therefore, it is difficult to know fundamentally whether those vegetables are cooked with only the processing time and texture. The appreciation of the food in terms of cooked or uncooked depends on an individual's sensory perception and expectation as the vocabulary can vary with the people's level of training, culture and their own eating habits. However, at any rate the applied cooking method must provide energy to the food sufficiently to activate physical and/or chemical reactions of the food's elementary compounds (ref). Thus, food is cooked when the reactions underlying the cooking of the foods are done. Thermodynamic, i.e., the states and transition states of the food compounds, with kinetics, i.e., the speed of the reactions, drive the cooking process (ref). The difficulty is to find the operational textural variables in phase with both the thermodynamic and kinetic variables of the reactions by which food engineers can tell quantitatively the onset and the end of the cooking reaction processes, or at least can identify the transitioning period between uncooked and cooked state.

In this work, the transitioning of the cowpea seeds to the cooked state was investigated. Cowpea (*Vigna unguiculata*) is a legume of multiple variety seeds which consists of a testa with a hilum and micropyle, two cotyledons and an embryonic axis (Swanson et al. 1985). The bean constitutes of moisture (5 - 15 %), proteins (20-26 %), carbohydrates, starch (40 - 70 %), fibre (3 - 5 %), and fat (1 - 3 %) (Khattab et al. 2009, Coffigniez et al. 2019, Adebooye and Singh 2007). Cowpea bean contains B-vitamins namely, thiamine (~0.9 %) and riboflavin (~0.15 %) (Edijala 1980, Phillips et al. 1988) and also some anti-nutritional components such as, tannins, and phytic acids which can precipitate proteins (Adebooye and Singh 2007, Khattab and

Arntfield 2009). During the cooking of the beans in hot water, the beans uptake water before starch gelatinization and protein denaturation occur. The flavor and color of the beans subsequently change with time but also with the number of the beans and the cooking media composition (Phillips et al. 1988). We hypothesis that the kinetics and all the reactions related to gelatinization of starch and denaturation of proteins would predominantly drive the cooking kinetics of cowpea seeds, given that protein and starch alone represent 60 % to 76 % of the total weight of the cowpea seeds. The water absorption can lead to substantial change of the beans' texture but it is not alone considered as cooking reaction, although it can be kinetically activated by heat. Thus, cowpeas beans may be considered cooked when they are gelatinized and/or denatured (ref).

The evolution of the mechanical properties of a system made with similar composition may be affected by those transitions of the beans' compound states. For instance, people in their own homes use essentially the finger test as mechanical test to assess the cooking levels (Voisey 1971). The finger test is used to evaluate how a product behaves mechanically when it is pressed between the fingers. A raw cowpea bean is shown in Fig. 1A. The state of cowpea bean after simmering at 95°C during 60 min and 90 min is shown in Fig. 1B and 1C respectively. Fig. 1D shows how the cowpea bean that has been simmered at 95°C during 90 min (shown in Fig. 1C) looks like after being crushed between the fingers. The beans are considered well-cooked when they can easily be crushed between the fingers, and this is the way Khattab et al (2009) have defined the cooking time (Khattab et al. 2009). Adebooye et al., 2007 pressed the beans between two glass plates after every 5 min and the time when the seed yielded was considered to be the cooking time (Adebooye and Singh 2007).



Fig. 1: A) Picture of a native black eye cowpea seed; and the seed after having been simmered for B) 60 min, C) 90 min in the water at 95 °C and D) shows the finger test applied on the seed of C).

According to Voisey (1971), the mechanical property is the most critical criteria for assessing the texture of food, because this has the strongest influence on the acceptance of food by people and is relevant to controlling mouth feeling (Mohsenin 1977, Ishihara et al. 2013). Texture analyser is used for this purpose to have a better control of the applied forces and precision of the food's mechanical responses, to recreate the conditions of consumer interactions with the food and to correlate those results to specific sensory texture attributes. In this work a mechanical compression test with a force precision of 10 mN was used in order to detect the state transition from uncooked to cooked period of the cowpea seeds when they undergo cooking processes. The aim of this study was to find out how the mechanical properties constants of cowpeas seeds' evolve between the beginning and the end of the reactions underlying its cooking.

2. Materials and Methods

2.1. Materials

The cowpea seeds were purchased from a local supermarket in Grenoble, France and used as such without additional treatment. A selection of the seeds based on visual appreciation criteria of the seed's surface homogeneity and cleanness was carried out and damaged seeds removed prior to the cooking method. More than 100 seeds were weighted separately using a precision Sartorius balance of 1.0 mg and the seed weight average was 0.200 g with the standard deviation of 0.023 g. The minimum and the maximum seed weight was 0.150 g and 0.249 g respectively.

2.2. Physical treatment: Soaking and heating to 95 °C

Four seeds were distributed in four 20 ml containers and filled with 2 g of deionized water to represent 1:10 (w/w). The containers were sealed and immediately heated to 95 °C in a water bath during 10, 30, 60, 75 and 90 min \pm 3 min. The cooking time was selected based on the findings by (Edijala 1980, Khattab et al. 2009, Coffigniez et al. 2019) who reported that at T \geq 95 °C the cooking time will vary from 35 to 90 min which depends on the type of seeds and the imprecision of the finger test. Additionally, the loss of solid matter is pronounced with the heating time. Therefore only the seeds that looked intact after they had been heated were selected for the study like the ones shown earlier in Fig. 1 (A, B, C). The initial weight (w_i) of each seed was recorded as well as the final weight (w_j) after heating. The amount in gram of water uptake per gram of cowpea seed termed R_{CS} was determined as:

$$R_{CS} = \left(w_f - w_i \right) / w_i \tag{1.}$$

 R_{CS} , water uptake ratio calculations were carried out using four seeds per heating time in quadruplicates. The temperature in the containers reached 60 °C and 95 °C in less than 2 and 5 min respectively.

2.3. Compression test

The test of compression was performed using the HAAKE MARS (Fig. 2a), Modular Advanced Rheometer System, Thermo Scientific instrument with a parallel geometry of 20 mm of diameter (TiLL11030P20). The measurement steps were managed with the HAAKE RheoWin Job manager software (add version). The zero gap was determined and the temperature was set to 25 °C, then the geometry was raised to 10 mm. A seed was placed for each measurement between the geometry and the plate then a first step program was run to bring the geometry onto the surface of the seed (Fig. 2b). The instrument geometry stopped going down when it measured a force of 25 mN.

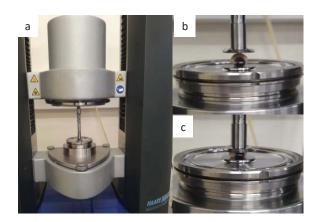


Fig. 2: Picture of the experimental instrument (a) to show the onset of the compressive test (b) and the deformation of the seed under the compression (c)

The force was reset to 0 at the current height, geometry position, or before the start of the compression test, the geometry position was taken as the initial height (h_0) of the seed. The height position of the geometry (Fig. 2c) during the compression (h_t) was recorded and the deformation (ε_t) at time t was calculated as:

$$\varepsilon_{t} = (h_{0} - h_{t})/h_{0}$$

Three determinations of the initial height are shown on the Fig. 3a. The forces detected by the instrument fluctuated below 10 mN when the geometry ran freely, but at the moment it touched the seed the force increased sharply and stopped at 25 mN, then the force was immediately reset to zero, before running the compression test program. Two types of programs were edited to study the compression of the seed. The first program (insert of Fig. 3b) was applied to investigate the deformation of the seeds over 1 h at a constant load force. The second was a multi-step loading program that consisted of a step-by-step increment of the force during the compression (Fig. 3b). This type of step-loading creep test was used by Mittal and co-authors to characterize the rheological property of the apple cortex (Mittal et al. 1987).

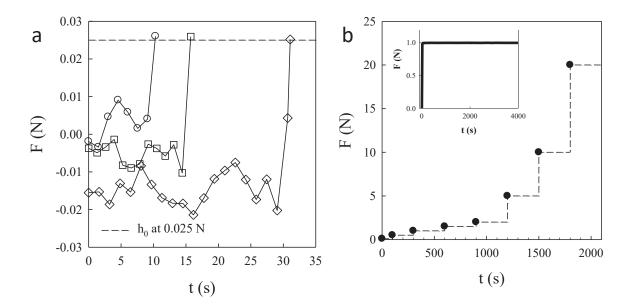


Fig. 3: a) Initial height position detection test repeated 3 times (open circle, square and diamond) shown as time dependence of the force during the course of the geometry toward the surface of the sample. The surface is detected when the force reaches $0.025 \, \text{N}$. b) Multiple step force program of the compressive test, the insert shows the long-time compressive test program for $F = 1 \, \text{N}$.

The compression tests were repeated four times using four seeds per heating time to give the strain plot that is the average of these four tests and its error bar is \pm the standard deviation.

2.4. Data analyses

Over the past three decades, some authors have investigated the uniaxial compressibility of food products in the characterization of food texture and recently Kiani Deh Kiani et al (2009) have presumably applied the compression test at ambient temperature to determine the elasticity of red bean grains as a function of their moisture content, i.e. not in cooking conditions (Finney et al. 1964, Mohsenin 1977, Kiani Deh Kiani et al. 2009). The time-dependence of strain with constant stress also termed creep function on the heating time is a more practical way to follow the solid-gel transition of the seeds, because the strain is time-independent for the real solid material, but time-dependent for the gel (Voisey 1971). In the gel state and under constant stress, the seeds can behave mechanically as a solid in a short time but as a fluid in a long time. The critical time, i.e. when the behavior changes from solid-like to fluid-like, is referred to as the yield time and it has been shown that this time for polymer and colloidal gel systems is stress-dependent (Sprakel et al. 2011). Cowpea seeds are heterogeneous and the area on which the force is applied is unknown. Moreover, the contact area between the probe and the seed expands under large deformation compression forces. The factors affecting the determination of Young's modulus as well as the elastic bulk modulus when agricultural products are subjected to compressive forces are documented (Mohsenin 1977, Finney et al. 1964, Hammerle and McClure 1971, Hamann et al. 2006). Owing to those factors, only the force and the deformation are recorded here to account for the seed viscoelasticity when evaluating the cooking levels of the seeds. Since this implies that the seeds have identical dimension to make meaningful comparison between samples of different heating times (Voisey 1971), the analysis is based on the fact that the variation of the seed apparent area (S) and Young's modulus (E) depend strictly on the heating time. Consequently, the product ExS yields a quantity termed elasticity index, K_e, in Newton unit (N), because its evolution results from E. K_e evolution is strictly the result of the heating, which could make it possible to distinguish the uncooked and cooked cowpea seeds. The Poisson's ratio is odd in large deformations of food products (Voisey 1971, Kiani Deh Kiani et al. 2009).

The compression test at 1.0 N of a seed soaked in demineralized water and heated for 10 min is presented in Fig. 4. The height of the seed decreased sharply at first exponentially then asymptotically over the critical time. The insert of the Fig. 4 shows the force profile with a dash line to represent the time it takes for the instrument to load the force. The time evolution of the height during the loading stage is the result of the coupling between the loading activity and the viscoelastic response of the material. This stage could be affected by the loading speed capacity of the instrument, therefore one should keep in mind that it is not only the seed response but it could also be an experimental imperfection. However, this loading phase is fundamental for understanding the behavior of the sample afterward. For a perfectly elastic material for instance, the loading stage would not be critical, because the elastic constant is time-independent. However, viscoelastic materials above yield stress have demonstrated time-dependent mechanical behavior (Nussinovitch et al. 1990, Mittal et al. 1987, Kiani Deh Kiani et al. 2009). Since the current sample subsequently exhibited flow behavior, it cannot be excluded that the force-loading rate influences the sample's microstructure and consequently the flow property. The experimental condition could have been difficult, if the samples have experienced severe aging in the time interval of the measurement albeit aging should contribute to increase the stiffness (ref?).

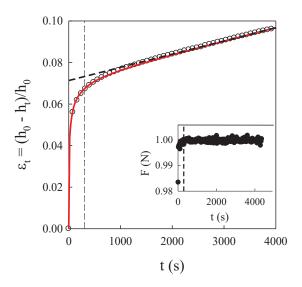


Fig. 4: Time dependence of deformation ε_t of a cowpea seed after heating the seed at 95 °C during 10 min as a result of loading 1 N force (insert). The vertical dash line is the time where the force is reached. The continuous line through the data is the fit to equation (1) with ω the slope of the dash line like the asymptote of the creep evolution ($\omega t^{\beta} + \varepsilon$), and ε is where the asymptote crosses the time 0 axis. The fit parameters are: $t_c = 23$ s, $\alpha = 0.35$, $\beta = 1$, $\varepsilon = 7.13$ %, $\omega = 6.35 \times 10^{-6}$ s⁻¹.

The time necessary for a material to undergo phenomena of disorganization and to start to flow depends on several factors that excite the curiosity of many authors (Sprakel et al. 2011, Coussot 2014). The deformation here showed a good coefficient of linear correlation with the forces during the force-loading period, but its consistency was highly time-dependent (Fig. 5). The linear response domain of the cowpea seed seemed to increase with increasing loading rate. Elsewhere, Kiani Deh Kiani et al (2009) found that the Young's modulus of red bean seed increased with increasing loading rate (Kiani Deh Kiani et al. 2009). With the exception of the imperfection experimental instrument (Voisey 1971) these observations are the results of time-dependent disorders or phenomena of changing of state which occurs in food materials as soon as they have been strained (Coussot 2014).

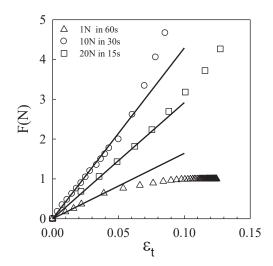


Fig. 5: Deformation dependence of loading forces on seeds after heating at 95 °C during 10 min. The forces and the times it takes to load the forces are indicated in the legend. The seeds respond elastically in the beginning of the loading force. The higher the force that is loading, the faster the loading process and the higher the elastic deformation domain. This observation reflects the impact of the loading rate on the compliance of the samples.

These disorder phenomena convert part of the working energy to entropy energy, the conversion time depends the kinetic of the reactions' mechanisms (ref). The material exhibits apparent elastic property if the increase of the load rate compensates the loss of energy. If the loading is done faster than the relaxation time of the material, then the material tends to behave like a perfect solid. Interestingly, the samples in this study exhibit a constant flow rate defined by the slope of the asymptote in Fig. 4. A similar creep curve was found with gellan gel by (Nussinovitch et al. 1990). This means that, if a linear relationship between the applied force and the flow rate is verified, then a quantity in N.s unit reflecting the viscosity of the material could be determined. This quantity is referred to as the viscosity index, K_{ν} . The applied force was plotted against the sample flow rate after performing the compression test at different constant forces. However, the result was noisy which was likely due to the fact that a new seed prepared in the same condition was loaded onto the rheometer when the applied force was

changed. The three plots of the Fig. 5 clearly demonstrate the impact of the physical characteristic of the seeds on the reproducibility of the data, given that the elastic index, K_e , corresponding to the three seeds of identical preparation yielded 16.42 N, 42.9 N, and 29.17 N with an average of 29.5 \pm 13 N. We believe that the native composition and the dimensions of the seeds could be the main causes of the noise as these affect the axial deformation. Indeed, the error on the deformation, $d\epsilon$, can be expressed as the sum of errors due to:- i) the applied forces, $d\epsilon_F$, as instrumental imperfection; ii) elastic modulus (E), $d\epsilon_E$, as the variation of the seed composition; and (iii) the area (S) over which the applied forces are distributed, $d\epsilon_S$ as the seed dimensions. If the elastic modulus of the seeds is assumed identical and the errors on the applied force are neglected then the error on the deformation is geometrical as

$$d\varepsilon = d\varepsilon_S = \left(\frac{dS}{S}\right) \cdot \varepsilon$$

Although the precise values of the elastic modulus is somewhat uncertain, the creep behavior for mostly all the samples is quite clear. Given that mostly all the samples tested in this study displayed the same creep behavior, we tried the model of Eq.(4) to sort out some characteristic parameters for the discussion on the mechanical properties of these complex systems. The strain was calculated and then the plot was fitted to Eq.(4) to obtain the values of the fit parameters.

$$\varepsilon_{t} = (\varepsilon_{0} - \varepsilon) \cdot e^{-N_{t}} + \omega \cdot t^{\beta} + \varepsilon$$

$$4.$$

with
$$N_t = (t/t_c)^{\alpha}$$

The fit function, Eq. (4), is a combination of the first period where the response of the material to the loading force is elastic-like, and the second period is the flow (creeping) at constant force. The t_c in the N_t , Eq. (5), gives the characteristic compliance time during the loading phase. The flow of the material takes place in this case following disorder events occurring during

compliance. The α in N_t is time structural factor of disordering events that occur in the material. The events can occur from time to time instead of being continuous as the internal dynamics are very weak to consider that they occur freely. The parameter ϵ_0 defines the initial condition of the deformation. For the flow part of the function, ω and ε are the constants of the regression function when applicable and they mean the flow rate and the axial deformation of the seed respectively. The constant ε is represented by the intersection between the y-axis and the function $\omega t^{\beta} + \varepsilon$ at t_0 , so ε is somehow the onset of the elastic response to the applied constant load. The adjusting parameter β can take 1 for all the analysed measurement, but if necessary, a value between 0.95 and 1 was tested to have the best adequacy with the measurement. Unless otherwise indicated, the value of β is 1. For the current samples, the Fig. 4 shows the adjustment and the regression function of the flow part. Both functions are plotted in solid and dashed lines respectively. The values of the adjustment parameters are also indicated in the legend. The flow rate, ω , of the seed was found to be 6.35×10^{-6} s⁻¹. The current seed felt like hard chewing gum when pressed between the fingers implying that the seed in this state is not yet ready to be eaten (ref).

3. Results and discussion

3.1. Deformation under incremental compressive forces

The average of the strain from the measurement of the 4 seeds after 10 min in water at 95 °C is shown in Fig. 6a. The standard deviation per the average strain yields a value δ that fluctuate between 10 % and 50 %. The median of δ values yields 30 %, i.e. 50 % of δ values are below 30 % and 50 % of δ values are above 30 %. This fluctuation was also observed for all the other quantities that were determined (i.e. viscosity indices, elasticity indices, flow rate, etc.). Therefore, unless otherwise indicated, considering a quantity Ψ of the mechanical tests, the standard deviation of the average can be taken as 30 % of the average in this present study. For

the sake of clarity, only the averages of the strain-time plots are displayed in Fig. 6b. The plots were analysed using the fit function (full line), the dash lines show the linear regression function of the flow part of the samples and the points where they meet the time 0 axis. The time delay between the forces (dotted lines) was decided according to the previous tests on the samples of the same series and the compression test program was adjusted to fit with the samples' behavior.

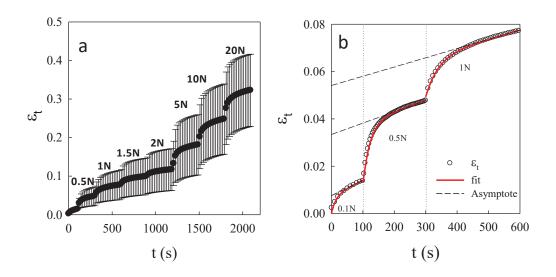


Fig. 6: a) Time dependence of deformation ε_t of a cowpea seed after heating the seed at 95 °C for 10 min as a result of loading multiple forces. The error bars are the standard deviation calculated on the average of 4 seeds. b) is the zoom in the 0.1 N, 0.5 N and 1 N to show the fit to equation (1) and the crossing point of the asymptote with the time 0 axis. For the error bars of Fig. 6b see Fig. 6a or apply 30 % × ε_t to get the standard deviation.

The cowpea seeds reacted instantly as an elastic material when the applied force was increased before going under constant flow rate a few seconds after the forces have reached the plateau. It is noteworthy mentioning that the time delay between the forces was not changed (increased for instance) to see the impact of this on the behavior of the samples. This will be tested in another study.

The compression test was carried out in an unconfined state, so the seeds expanded transversally by the flow behavior but not as an incompressible fluid. There are a number of factors that can make the compression to stop. These are - i) when locally the concentration increases and the compressibility of the seeds decreases as the volume decreases towards the total volume of the uncompressible elementary constituents. The deformation of the seeds will be stopped by the exclusion effect of the elementary constituents, i.e. limit of the samples compressibility; ii) when the geometry reaches the zero gap. The measurements did not show any remarkable tendency towards stability which means that the maximum degree of compaction was not attained for all the mechanical tests. The time between the application of load and the moment when the sample yields which is the yield or critical time, generally depends on the applied force because yielding mechanism are an activated energy process. The critical time and stress relationships vary from one system to another. It depends on the competition and the cooperative or synergistic effects of the many yielding events that can take place in the seed at any instant. The thermal motion of small molecules and reptation of biopolymers (De Gennes 1976), the balance between the dynamic of physical bonds rupture and reconstruction (Sprakel et al. 2011) are some of the fundamental yielding events of which the kinetics determine the critical time of the creep behavior of the samples.

The critical time, t_c , and α of the fit function are related to the time behavior of the sample under yielding. The values of α fluctuate between 0.5 and 1 when the values of t_c fluctuate between 14 s and 70 s with the change of the applied forces. This means that a clear correlation between the parameter α or t_c with the applied forces was not observed in the present study. Thus, it was not possible to correlate afterward the critical time with the heating time of the seeds and this implies the complexity of characterizing the yield time of heterogeneous condensed materials under mechanical stress. For instance, it is demonstrated that the relaxation time of polymer and colloidal systems exhibit an exponential decay dependence on the applied stress (Sprakel

et al. 2011), but for a mixture of polymer and colloidal system or for heterogeneous systems in general this relationship is not fundamentally confirmed. Cowpea seed systems consist of a tightly wrapped packs of starch granule cells in a protein matrix around which there are hydrocolloids and low presence of fat (Swanson et al. 1985, Coffigniez et al. 2019). The compression test of this system has shown yielding despite of the applied forces (between 100 mN to 20 N) demonstrating the weakness of the energy needed to activate the yielding mechanisms. The absorption of water by the seeds which causes the microstructure to swell and the intercellular spaces to increase is pronounced by heat, capillary effects, and by the pectin and protein based substances through the migration process in order to balance the osmotic pressure (Coffigniez et al. 2019). Although the appearance of the whole seed seemed to be preserved, some of the walls of the interfacial cells could have been damaged and water may continue to diffuse into the whole seed until the osmotic pressure is balanced even at room temperature. The dynamic of the system to reach equilibrium would have been enhanced by a local increase of temperature due to the effects of stress. The lubrication of the interstitial spaces between the seeds cells and their large clusters due to the presence of lipid substances in the intercellular spaces would be also enhanced by the locally induced increase of temperature by stress. It is noteworthy to mention that after 10 min in water at 95 °C the seeds have taken on average about 0.4 ± 0.3 g of water per gram of seeds.

3.2. Compressive force and deformation relationships upon heating time

It is shown earlier (in Fig. 5) that the instantaneous responses of the samples are elastic before the elastic response of the sample give way to flow response when the imposed forces are completely loaded. Therefore, the intersection between the (asymptotic) flow function and time 0 axis is taken here as the instantaneous elastic deformation, ε , and assigned to the applied force. Fig. 7 shows the results for different heating times at 95 °C and time 0 for the uncooked (native cowpea) beans, which is denoted as NC.

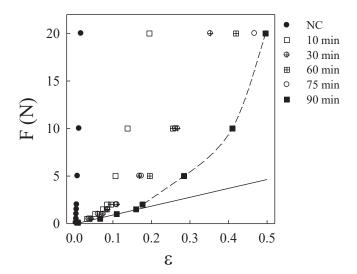


Fig. 7: Applied forces as function of the deformation ε for the native cowpea seed (NC) and the different times of heating the seeds at 95 °C. The full line through the data shows the elastic domain for the seeds after heating at 95 °C during 10 min and the slope reflects the elastic constant in N unit. The dash line is a guide for eyes. Apply 30 % × ε for horizontal standard deviation.

The force as the functions of deformation increases quite linearly as shown by the full line through the data of 90 min and deviates from linearity with higher slope. The compression tests of alginate gels have shown practically similar trend, which the authors have described by a concave upward function using a power-law model, where the pre-factor was referred to as the gel stiffness and the power as the degree of concavity that reflects the deviation from linearity. When the power equal 1, then the power-law model reduces to Hooke's law and the pre-factor coincides with the modulus of elasticity (Mancini et al. 1999). Given that the slope is characteristic of the seeds elasticity, the increase of this means strengthening of the seed. However, under unconfined compressive force, this trend may reflect the compaction effects requiring additional force to strain the sample rather than strain hardening effects (Mancini et al. 1999). Furthermore, the resistance to stretch the seed coat could explain the rising of the force-deformation function. At higher compressive forces, the deformation amplitude decreases

from the native seed with increasing heating time. However, the way it decreases seems to depend on the applied forces.

Fig. 8 shows for each applied force the deformation values as a function of the heating times. The results in this figure mimic taking one seed after the other for each heating time and crushing it between fingers or teeth to check whether the seeds are cooked or not. The scale of A to C shown on the top axis of Fig. 8 represents how the seed felt between the fingers or teeth where:- A = Uncooked or not edible; B = cooked a little but firm on teeth, i.e. "al-dente"; C = cooked or well-done, i.e. melt in mouth.

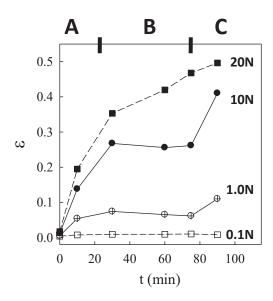


Fig. 8: The deformation of the Fig. 7 is plotted as a function of the heating time at 95 °C when the forces indicated in the Figure are applied. The finger test A, B, and C on the top axis represent how the cowpea seed was perceived by different people where A = Uncooked or not edible; B = cooked a little like firm on teeth, i.e. "al-dente"; C = cooked or well done. Apply 30 % × ε for vertical standard deviation and ± 3 min for horizontal (time) error bars.

At a weak or strong applied forces, i.e. 0.1 N or 20 N, the deformation of the seed evolves without a significant discriminative signature between the cooking levels. For the curve of 20 N, the change of the slope is weak between A and B and is absent between B and C. For the

curve of 0.1 N, the deformations are too weak to provide relevant information on the periods of the cooking reactions. Therefore, the sort by cooking-level of the seed is weakly precise with both extreme forces. However, for intermediate compressive forces, the test shows a remarkable transitional phase that is characterized by a plateau between level A and C. The controlling compressive forces show a clear-cut between uncooked and cooked seeds as long as the compression test is done with moderate applied forces.

3.3. Compressive deformation rate and the seed viscosity index

The deformation rates (ω) of the seeds are plotted as function of the applied forces to the different heating times. Four graphs are displayed in Fig. 9 to illustrate the force-dependence of ω. These graphs are; the raw seed (NC, Fig. 9a) and the seed after heating time of 10 min (Fig. 9b), 60 min (Fig. 9c) and 90 min (Fig. 9d) at 95 °C. The graph of the native seed shows no deformation rate for the lowest compressive forces whereas ω starts increasing from roughly 1 N (Fig. 9a). The rise of ω from a stress threshold could characterize the heated seeds too, although it is not seen in the figures 9 b, c, and d, which is mainly attributed to the fact that the yield stress is lower than the forces applied in this case. Indeed, the overall seeds exhibit timedependent yielding behavior which energy barrier stem from the physical bonds that provide to the seeds the resistance against flow under their own weight. The fact that ω decreases first for the seeds of Fig. 9 b, c, d suggests that free liquid exuded out of the seeds cell interstices. Such expulsion leads to compaction as a result of which ω decreases to a minimum that reflects presumably the transition between the liquid removal and a jamming flow regime. In the jamming regime, ω increases from the minimum around 30 ± 10.10^{-6} s⁻¹ to a maximum around 75 ± 10.10^{-6} s⁻¹ with increasing applied forces (N) for the heated seeds but the maximum for the native seeds was not reached. The ω of the native seeds is 10 to 20 times lower than that of the heated seeds. The deformation rate is assumed to evolve with the applied forces linearly in

the jamming flow regime. This assumption made it possible for the viscosity index, K_{ν} , to be calculated.

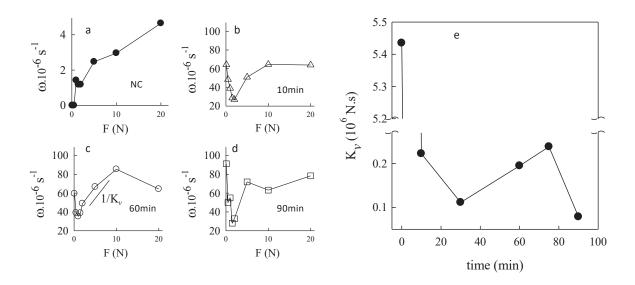


Fig. 9: Force-dependence of deformation, ω , of native cowpea (a), heating times in the Figures (b, c, d) at 95 °C reflect the evolution of the seeds viscosity (K_v in N.s unit) as a function of the heating time, time 0 is NC, (e). K_v is given by considering ω as linear with F in the increasing (jamming) domain. Note that the break on the y-axis shows the amplitude of the loss of the K_v of the cowpea once it starts to cook and the time domain where K_v increases and this shows the transitioning between uncooked and cooked state. Apply 30 % × (K_v , ω) for vertical standard deviation and \pm 3 min for horizontal (time) error bars.

The compressive viscosity index, K_{ν} , decreases catastrophically between the native seeds and the seeds after 10 min of heating. The decrease continues weakly between 10 min and 30 min heating time and rises between 30 min and 80 min, where presumably:- (i) gelatinization of starch (Kong et al. 1999, Biliaderis et al. 1980, Adebooye and Singh 2008); (ii) denaturation with aggregation of protein (Tolkach and Kulozik 2007); (iii) and hydration of carbohydrate like pectin, significantly take place (Coffigniez et al. 2019). At the end of these processes, after

80 min, the K_{ν} decreases continuously because of additional absorption of water (Fig. 9e) until the seeds are bursting.

3.4. Seeds' stiffness and flow rate as function of the heating time

The relation between ε and the applied forces were interrogated to derive the elastic coefficient according to Hooke's law termed elasticity index, Ke in N unit. The Ke is the constant of proportionality between the applied forces and the deformation in the elastic like domain, i.e. before the deformation deviates from linearity. The Ke values are plotted as function of the heating time (result of native seeds is represented by time zero) on the left axis of Fig. 10a in a log-lin scale. The deformation rates, ω, at 0.1 N are plotted on the same figure (Fig. 10a) as function of the heating time using the right axis. The cooking level A, B, C are presented on the top axis of the heating time. The Fig. 10b shows the evolution of the water uptake by the seeds. During the first 10 min, the elasticity index, K_e, of the seeds decreases steeply from 560 N to 19 N, a loss of 97 % of their initial stiffness owing to the flow of water into the seeds macrostructure. The water uptake by the seeds during the first 10 min was on average 38 % of the seeds weight. As a result of this absorption of water by the seed, the flow rate of the seeds significantly increased. When the heating time was increased from 10 min to 30 min, the seeds lost 36 % of their stiffness and the seeds flow rate ω increased weakly. However the amount of water uptake by the seeds in this second period increased by 50 % with almost a constant rate. The decrease of the stiffness during the heating period from 10 min to 30 min is not a result of the absorption of water alone but also a consequence of a collection of mechanisms with opposing effects that prevent both the catastrophic decrease of the stiffness and thickness of the seeds. Thus, we suggest that the gelatinization of starch and denaturation of protein processes in this heating period strengthen the seeds. These processes define the onset of the

cooking rather than the water absorption alone. Therefore, it could be hypothesised that the cooking of the seeds starts between 10 min and 30 min at 95 °C.

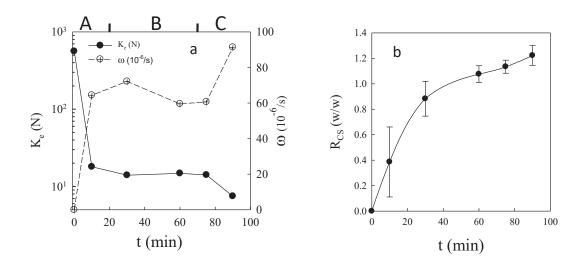


Fig. 10: (a) Evolution of the elasticity constant, K_e on the left axis, and the deformation rate (ω) on the right axis for 0.1 N as a function of the heating time of the seed at 95 °C. Apply 30 $\% \times (K_e, \omega)$ for vertical standard deviation and ± 3 min for horizontal (time) error bars. (b) Water uptake in w/w of cowpea seeds as function of the heating time at 95 °C. Error bars are \pm the standard deviation computed on 4 seeds for each heating time.

When the heating time was between 30 min and 80 min, the Ke remained practically constant at 14 N, although the absorption of water by the seeds was shown to slightly increase. We could say that the cooking reactions contribute to the stability of the Ke until the end of the reactions somewhere between 75 min and 90 min. Beyond 75 min the stiffness and the thickness of the seeds reduces catastrophically. Heating time longer than 90 min destroyed the seeds and their internal contents were expelled in the cooking media (ref).

4. Conclusion

Cowpea is rich in protein (20%-26% w/w) and starch (40%-70% w/w), it contains also vitamin, fat and hydrocolloids but in weak proportion. Cowpea seeds are multiple varieties of species of

which the size, weight, seeds coat texture and composition are the specific attributes. Seeds without visual defects were selected to investigate the seeds cooking time using the mechanical compression test given that the mechanical properties of food are correlated with the physical and chemical changes of the food. However:- i) how the seeds will behave when they are subjected to mechanical test; ii) how their mechanical properties are correlated with the seeds transformations; and iii) whether this correlation will allow independently food engineers to visualize the transitioning of the seeds to the cooked state cannot be predicted. The seeds are cooked when the physical and chemical reactions underlying the seeds cooking are done. Therefore, we think that the activation of both protein denaturation and starch gelatinization reactions are the starting point of the seed cooking, although before these reactions happen the seeds uptake water during cooking at 95°C. We found that cooking of the seeds starts between 10 min and 30 min because the seed's stiffness (elasticity index) and thickness (viscosity index) decrease weakly during this period of time. Before this period both mechanical constants decreased strongly, for instance a loss of 97 % the elasticity index was observed during the first 10 min of heating of cowpea seeds. The time the seeds are cooked was found to be between 75 min and 90 min, because in this period it was observed that both mechanical constants decrease sharply. Furthermore just before, i.e. between 30 min and 75 min, the stiffness was practically constant, and the thickness was increasing or the flow rate was decreasing. To get the stiffness (elasticity index) and the thickness (viscosity index), a stretched exponential plus a linear asymptotic time function was used to fit the creep behavior of the sample where the strain (ε) and the flow rate (w) were the fit functions parameters. These fit parameters correlate respectively with the applied forces within the linear regime. Viscoelasticity indices correlate with the cooking variation transitioning.

This work allow to investigate the influence of the cooking medium (salt, pH, sugar, etc.) and other physical seed treatment (from harvest to cooking) on the cooking time and the way the

legumes behave mechanically when the undergo cooking reactions in order to achieve commercially acceptable new foods textures with reduction of the cooking energy.

5. Acknowledgment

The authors declare no conflicts of interest. This work was financially supported by the educational ministry of TOGO. The Laboratoire Rhéologie et Procédés (LRP) is part of the LabEx Tec 21 (Investissements d'Avenir - grant agreement n°ANR-11-LABX-0030) and of the PolyNat Carnot Institut Investissements d'Avenir - grant agreement n°ANR-11-CARN-030-01).

6. References

- ADEBOOYE, O. C. & SINGH, V. (2007). Effect Of Cooking On The Profile Of Phenolics, Tannins, Phytate, Amino Acid, Fatty Acid And Mineral Nutrients Of Whole-Grain And Decorticated Vegetable Cowpea (*Vigna Uuguiculata L. Walp*). Journal of food Quality, 30, 1101-1120.
- ADEBOOYE, O. C. & SINGH, V. (2008). Physico-chemical properties of flours and starches of two cowpea varieties (*Vigna Unguiculata (L.) Walp*). Innovative Food Science and Emerging Technologies, 9, 92-100.
- BILIADERIS, C. G., MAURICE, T. J. & VOSE, J. R. (1980). Starch gelatinization phenomena studied by differential scanning calorimetry. Journal of Food Science, 45, 1669-1674.
- COFFIGNIEZ, F., BRIFFAZ, A., MESTRES, C., AKISSOÉ, L., BOHUON, P. & EL MAÂTAOUI, M. (2019). Impact of soaking process on the microstructure of cowpea seeds in relation to solid losses and water absorption. Food Research International, 119, 268-275.
- COUSSOT, P. (2014). Yield stress fluid flows: A review of experimental data. Journal of Non-Newtonian Fluid Mechanics, 211, 31-49.
- DE GENNES, P. G. (1976). Dynamics of Entangled Polymer Solution. Macromolecules, 9, 594-598.
- EDIJALA, J. K. (1980). Effects of processing on the thiamin, riboflavin and protein contents of cowpeas (*Vigna unguiculata (L) Walp*). I. Soaking, cooking and wet milling processes Journal of Food Technology, 15, 435-443.
- FINNEY, E. E., HALL, C. W. & THOMPSON, N. R. (1964). Influence Of Variety And Time Upon The Resistance Of Potatoes To Mechanical Damage. American Potato Journal, 41, 170-186.
- HAMANN, D. D., ZHANG, J., DAUBERT, C. R., FOEGEDING, E. A. & DIEHL, K. C. (2006). Analysis Of Compression, Tension, And, Torsion For Testing Food gel Fracture Properties. Journal of Texture Studies, 37, 620-639.
- HAMMERLE, J. R. & MCCLURE, W. F. (1971). The Determination Of Poisson's Ratio By Compression Tests Of Cylindrical Specimens. Journal of Texture Studies, 2, 31-49.

- ISHIHARA, S., NAKAO, S., NAKAUMA, M., FUNAMI, T., HORI, K., ONO, T., KOHYAMA, K. & NISHINARI, K. (2013). Compression Test Of Food Gels On Artificial Tongue And Its Comparison With Human Test. Journal of Texture Studies, 44, 104-114.
- KHATTAB, R. Y. & ARNTFIELD, S. D. (2009). Nutritional quality of legume seeds as affected by some physical treatments 2. Antinutritional factors. Food Science and Technology, 42, 1113-1118.
- KHATTAB, R. Y., ARNTFIELD, S. D. & NYACHOTI, C. M. (2009). Nutritional quality of legume seeds as affected by some physical treatments, Part 1: Protein quality evaluation. Food Science and Technology, 42, 1107-1112.
- KIANI DEH KIANI, M., MAGHSOUDI, H. & MINAEI, S. (2009). Determination of Poisson's ratio and Young's modulus of red bean grains. Journal of Food Process Engineering, 34, 1573-1583.
- KONG, C. S., OGAWA, H. & ISO, N. (1999). Compression Properties Of Fish-Meat Gel As Affected By Gelatinization Of Added Starch. Journal of Food Science, 64, 283-286.
- MANCINI, M., MORESI, M. & RANCINI, R. (1999). Uniaxial Compression And Stress Relaxation Tests On Alginate Gels. Journal of Texture Studies, 30, 639-657.
- MITTAL, J. P., MOHSENIN, N. N. & SHARMA, M. G. (1987). Rheological Characterization Of Apple Cortex. Journal of Texture Studies, 18, 65-93.
- MOHSENIN, N. N. (1977). Characterization And Failure In Solid Foods With Particular Reference To Fruits And Vegetables. Journal of Texture Studies, 8, 169-193.
- NUSSINOVITCH, A., AK, M. M., NORMAND, M. D. & PELEG, M. (1990). Characterization Of Gellan Gels By Uniaxial Compression, Stress Relaxation and Creep. Journal of Texture Studies, 21, 37-49.
- PHILLIPS, R. D., CHINNAN, M. S., BRANCH, A. L., MILLER, J. & MCWATTERS, K. H. (1988). Effects of Pretreatment on Functional and Nutritional Properties of Cowpea Meal. Journal of Food Science, 53, 805-809.
- SPRAKEL, J., LINDSTRÖM, S. B., KODGER, T. E. & WEITZ, D. A. (2011). Stress Enhancement in the Delayed Yielding of Colloidal Gels. Physical Review Letters, 106.
- SWANSON, B. G., HUGHES, J. S. & RASMUSSEN, H. P. (1985). Seed Microstructure: Review Of Water Imbibition In Legumes. Food Microstructure, 4, 115-124.
- TOLKACH, A. & KULOZIK, U. (2007). Reaction kinetic pathway of reversible and irreversible thermal denaturation of b-lactoglobulin. Lait, 87, 301-315.
- VOISEY, P. W. (1971). Modernization Of Texture Instrumentation. Journal of Texture Studies, 2, 129-195.